

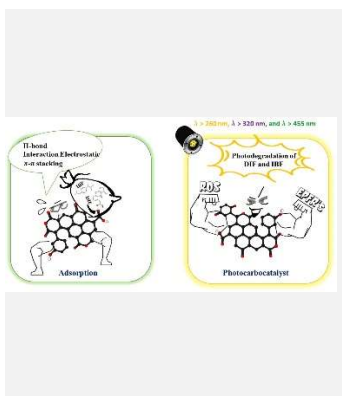
Can the biochar behave like a photocarbocatalyst? Quantitative and qualitative strategies to find out

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Activated carbon ($AC_{SSS}^{H_3PO_4}$), synthesized from sunflower seed shells (SSS) activated with H_3PO_4 (78% wt.), was evaluated as a photocarbocatalyst in the adsorption/degradation of diclofenac (DFC) and ibuprofen (IBP) using quantitative and qualitative strategies. We developed a quantitative and qualitative strategy to evaluate the degradation of DFC and IBP under light irradiation at different wavelengths. ATR-FTIR measurements (qualitative strategy) revealed that both pollutants adsorbed onto $AC_{SSS}^{H_3PO_4}$ underwent chemical changes after 5 h of light irradiation. The pollutants desorption from the irradiated $AC_{SSS}^{H_3PO_4}$ (quantitative strategy) and the further determination by UPLC showed that under irradiation at $\lambda > 260$ nm, $AC_{SSS}^{H_3PO_4}$ showed degradation of 62 and 30% for adsorbed DFC and IBP, respectively, after 5 h. In contrast, when the light at $\lambda > 320$ nm and $\lambda > 455$ nm was used, pollutant degradation dropped to 42-29% and 20%.

Introduction

Recently, some of us reported the optimized synthesis of activated carbon from sunflower seed shells activated with H_3PO_4 . This material exhibited a high surface area, diversity of bulky and surface functional groups, and high adsorption capacity of diclofenac and ibuprofen [1]. To our knowledge, there are no studies about using this kind of activated carbon as a photocarbocatalyst under UV and visible light irradiation for non-steroidal anti-inflammatory drugs (NSAIDs) degradation. Thus, the main aim of this study was to assess DCF and IBP oxidation on activated carbon under UV and visible light irradiation. Still, since this carbonaceous material exhibited significant adsorption (~98%) of both pollutants, we developed a strategy to evaluate qualitatively and quantitatively their photocarbocatalytic degradation.

Material and Methods

$AC_{SSS}^{H_3PO_4}$ was synthesized following the methodology reported previously [1]. Solutions containing 2.0 mg L^{-1} of DFC or IBP and 1.0 g L^{-1} of the activated carbon at pH 6.5 were stirred for 1 h in the dark. Samples were withdrawn at different times, filtered by PTFE filters (0.22 μm), and evaluated by (UPLC UltiMate 3000 Thermo Fisher). Then, these suspensions were irradiated using an Xe-lamp housing (New Port) and several cut-off filters ($\lambda > 260$ nm, $\lambda > 320$ nm, and $\lambda > 450$ nm). Pollutant extractions were carried out by suspending the irradiated $AC_{SSS}^{H_3PO_4}$ samples with

acetonitrile/water solutions under constant magnetic stirring for 24 h. The process was repeated three times. Then, the solid was separated, and the solutions were filtered. Finally, they were injected into UPLC equipment to determine the concentration of DFC and IBP.

The ATR-FTIR measurements were carried out using a Perkin-Elmer FT-IR spectrometer equipped with an attenuated total reflectance (ATR) using 1.0 g L^{-1} of $AC_{SSS}^{H_3PO_4}$ in solutions containing 50.0 mg L^{-1} of both pollutants. The suspensions were irradiated using the same conditions mentioned above. Solids were separated by centrifugation and dried at 60 °C for 24 h in a vacuum oven.

Results and Discussion

Characterization of synthesized activated carbon was performed through a multi-technique approach. DRS spectrum of $AC_{SSS}^{H_3PO_4}$ showed that this material exhibits light absorption in the whole UV and visible region (200-800 nm) (Figure 1a). At the same time, SEM micrograph and X-ray tomography images revealed porous features and channels from lignin in the original biomass structure. FT-Raman spectrum (insert Figure 1a) showed G and D bands whose I_G/I_D ratio was around 0.79, exhibiting a high graphitization degree ($I_D/I_G < 1$). Observing the deconvolution of the XPS C 1s spectrum (Figure 1c), it is possible to identify adventitious carbon or C-H, C-O, C=O, and π -stacking satellites from graphitic structures, respectively. The XPS P 2p spectrum (Insert Figure 1c) and its deconvolution showed the

presence of two components due to C-P-O and C-O-P bonds, respectively [1]. The FTIR spectrum (Figure 1b) exhibited several bands compatible with P-O, P=O, HO-P=O bonds, aromatics, phenols, quinones, and carboxyl groups.

The EPR spectrum taken at 77 K revealed (Figure 1d) an intense signal with a g-factor of 2.001 and a value of 4.86×10^6 spins g^{-1} compatible with carbon-centered EPFR with graphitic nature.

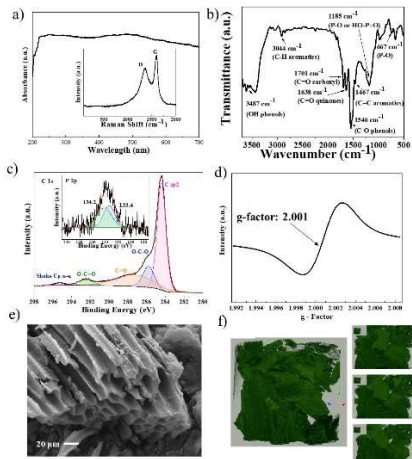


Figure 1. Characterization of $AC_{SSS}^{H_3PO_4}$ material (a) DRS and insert FT-Raman spectra (b) FTIR spectrum (c) XPS of C1s signal and insert P 2p (d) EPR at 77 K. (e) SEM micrograph and (f) 3D X-ray tomography.

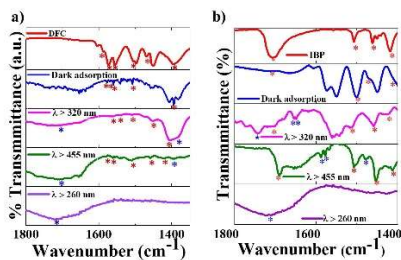


Figure 2. Qualitative determination of the degradation of (a) DFC and (b) IBP by ATR-FTIR.

The qualitative strategy to find out if both pollutants were or not degraded under light irradiation was achieved using ATR-FTIR measurements (Figure 2).

Conclusions

$AC_{SSS}^{H_3PO_4}$ material exhibited a significant capacity to adsorb DFC and IBP, degrading them under UV and visible light.

References

[1] J.J. Alvear-Daza, A. Canneva, J.A. Donadelli, M. Manrique-Holguín, J.A. Rengifo-Herrera, L.R. Pizzio. *Biomass. Convers. Biorefin.* 13 (2023) 13197.

These revealed that DFC and IBP were adsorbed on the surface of $AC_{SSS}^{H_3PO_4}$. When the activated carbon was irradiated with light at $\lambda > 260$ nm, the IR of DFC and IBP disappeared, and other news at 1718 cm^{-1} (blue asterisk), probably due to oxidized byproducts, emerged. Under irradiation at $\lambda > 320$ and 455 nm, partial DFC and IBP degradation was found.

The extraction of pollutants and their oxidized byproducts was performed with acetonitrile/water solutions, recovering 96% and 94% of DFC and IBP, respectively. Results under irradiation showed that under light at $\lambda > 260$ nm, $AC_{SSS}^{H_3PO_4}$ showed degradation of 62 and 30% for adsorbed DFC and IBP, respectively, after 5 h. In contrast, when the light at $\lambda > 320$ nm and $\lambda > 455$ nm was used, pollutant degradation dropped to 42-29% and 20% (Figure 3a). Chromatograms obtained after 5 h of irradiation (Figures 3b and 3c) showed the presence of new peaks probably attributed to oxidized byproducts.

Due to its high specific surface area, detecting DMPO-OH adducts by ESR-spin trapping was unsuccessful. However, we realized EPR experiments at 77K under in situ irradiation at different wavelengths (Figure 4). The signal with g-factor 2.001 increased under light irradiation, obtaining values of 8.0×10^6 spin g^{-1} for all the wavelengths.

Figure 3. (a) Quantitative determination of DFC and IBP degradation and its chromatograms for (b) DFC and (c) IBP after 5 h of irradiation.

We concluded that reactive oxygen species (ROS) produced in $AC_{SSS}^{H_3PO_4}$ pores, where C-centered EPFRs could be involved, would be responsible for DFC and IBP degradation.

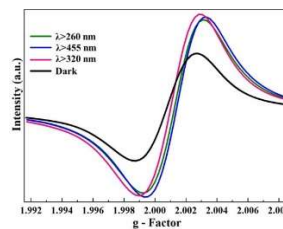


Figure 4. EPR spectrum at 77 K of $AC_{SSS}^{H_3PO_4}$ material irradiated by different wavelengths.